



Solar photoassisted anodic oxidation of carboxylic acids in presence of Fe^{3+} using a boron-doped diamond electrode

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ABSTRACT

This paper reports a comparative study on the anodic oxidation of 2.5 l of 50 mg l⁻¹ TOC of formic, oxalic, acetic, pyruvic or maleic acid in 0.1 M Na₂SO₄ solutions of pH 3.0 with and without 1.0 mM Fe³⁺ as catalyst in the dark or under solar irradiation. Experiments have been performed with a batch recirculation flow plant containing a one-compartment filter-press electrolytic reactor equipped with a 20 cm² boron-doped diamond (BDD) anode and a 20 cm² stainless steel cathode, and coupled to a solar photoreactor. This system gradually accumulates H₂O₂ from dimerization of hydroxyl radical ($\cdot\text{OH}$) formed at the anode surface from water oxidation. Carboxylic acids in direct anodic oxidation are mainly oxidized by direct charge transfer and/or $\cdot\text{OH}$ produced on BDD, while their Fe(III) complexes formed in presence of Fe³⁺ can also react with $\cdot\text{OH}$ produced from Fenton reaction between regenerated Fe²⁺ with electrosynthesized H₂O₂ and/or photo-Fenton reaction. Fast photolysis of Fe(III)-oxalate and Fe(III)-pyruvate complexes under the action of sunlight also takes place. Chemical and photochemical trials of the same solutions have been made to better clarify the role of the different catalysts. Solar photoassisted anodic oxidation in presence of Fe³⁺ strongly accelerates the removal of all carboxylic acids in comparison with direct anodic oxidation, except for acetic acid that is removed at similar rate in both cases. This novel electrochemical advanced oxidation process allows more rapid mineralization of formic, oxalic and maleic acids, without any significant effect on the conversion of acetic acid into CO₂. The synergistic action of Fe³⁺ and sunlight in anodic oxidation can then be useful for wastewater remediation when oxalic and formic acids are formed as ultimate carboxylic acids of organic pollutants, but its performance is expected to strongly decay in the case of generation of persistent acetic acid during the degradation process.

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1. Introduction

A large variety of powerful oxidation methods grouped under the name of advanced oxidation processes (AOPs) has been recently proposed for the degradation of toxic and/or biorefractory organics in wastewaters [1–3]. They are environmentally friendly techniques based on the in situ generation of hydroxyl radical ($\cdot\text{OH}$), which has a high standard reduction potential ($E^\circ(\cdot\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V vs. NHE}$) allowing its non-selective reaction with organics giving rise to dehydrogenated or hydroxylated derivatives that can be in turn totally mineralized, i.e. converted into CO₂. In these processes, however, a mixture of carboxylic acids (usually formic, oxalic and acetic) are formed as ultimate by-products and

their hard destruction with $\cdot\text{OH}$ largely prolongs the mineralization time with the consequent efficiency loss and/or greater operation cost of the treatment [4–21]. A clear improvement of the removal rate of these compounds is found for photoassisted AOPs [2–6,9,10,14–16,18,21] and then, more research efforts are needed to develop cheap solar driven techniques using solar photons of wavelengths longer than 300 nm as free and renewable energy source.

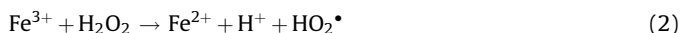
One of the most popular AOPs is the Fenton method [2,3,9,12,19], where a mixture of Fe²⁺ and H₂O₂ is added to an acidic wastewater to produce $\cdot\text{OH}$ and Fe³⁺ from Fenton reaction (1), which achieves its maximum rate at pH 2.8 [22] with a second-order rate constant (k_2) of 63 M⁻¹ s⁻¹ [23]:



The Fe³⁺/Fe²⁺ system is catalytic and Fe²⁺ can be regenerated in very small extent from the reduction of Fe³⁺ by H₂O₂ from the

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Fenton-like reaction (2) with $k_2 = 8.4 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ [24]:

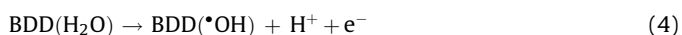


However, the formation of very stable Fe(III) complexes with final carboxylic acids makes this process rather inefficient. Under UV or solar irradiation, so-called photo-Fenton method, the degradation of organics is enhanced [2–5,9,18] from: (i) the photolysis of the $\text{Fe}(\text{OH})^{2+}$ complex, the predominant species of Fe(III) at pH 2.5–5.0 [25], by the photo-Fenton reaction (3) [26]:



where more oxidant $\bullet\text{OH}$ is directly generated and greater amount of Fe^{2+} is regenerated, thus accelerating the rate of reaction (1) in presence of H_2O_2 and (ii) the photodecomposition of complexes formed between Fe(III) and oxidation by-products such as oxalic and other carboxylic acids [26–29]. The fast photolysis of Fe(III)-oxalate complexes ($\text{Fe}(\text{C}_2\text{O}_4)^+$, $\text{Fe}(\text{C}_2\text{O}_4)_2^-$ and $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$) in presence of O_2 also involves the parasitic generation of H_2O_2 producing more quantity of $\bullet\text{OH}$ from Fenton reaction (1). This behaviour has been well-proven from the mediated degradation of several organic pollutants with Fe(III)-oxalate ions under solar irradiation [30–33].

Electrochemical advanced oxidation processes (EAOPs) are also receiving increasing attention for wastewater remediation. The most common EAOP is anodic oxidation (AO) in which organic pollutants are destroyed with $\bullet\text{OH}$ formed at the surface of a high O_2 -overvoltage anode such as a boron-doped diamond (BDD) thin film from water oxidation by reaction (4) [8,12,34–37]:



This anode material is preferred in AO because it interacts very weakly with $\bullet\text{OH}$ resulting in a much greater O_2 -overvoltage than other conventional anodes and in an enhancement of organic removal with reactive $\text{BDD}(\bullet\text{OH})$ [36]. This behaviour has been confirmed by the effective mineralization of short carboxylic acids such as formic [38,39], oxalic [38–42], acetic [38,43–45], pyruvic [37] and maleic [39,43,46] from electrolysis with a BDD electrode.

The high oxidation power of BDD also allows the production of other weaker oxidants such as reactive oxygen species (ROS) like H_2O_2 and ozone, as well as peroxo-derivatives coming from the oxidation of the anion of the background electrolyte [34–37]. However, the role of all these species for increasing the efficiency of the degradation process of organic pollutants has been disregarded. In this scenario, an interesting possibility could be to profit from the potential oxidant power of electrogenerated H_2O_2 via solar photo-Fenton. To assess the viability of this novel environmentally friendly EAOP, we have undertaken a comparative study on the AO process of common carboxylic acids in acidic aqueous media with Fe^{3+} combined with solar irradiation. This paper reports the results obtained for the comparative treatment of 50 mg l^{-1} of total organic carbon (TOC) of formic, oxalic, acetic, pyruvic and maleic acids by AO with and without Fe^{3+} and by the proposed solar photoassisted AO in presence of Fe^{3+} . All trials were carried out in a small batch recirculation flow plant with an undivided BDD/stainless steel cell coupled to a solar photoreactor operating under steady conditions. A concentration 1.0 mM of catalytic Fe^{3+} was added to the tested solutions to ensure the formation of Fe(III)-carboxylate complexes in large extent. The ability of the flow plant to degrade these species under Fenton-like and solar photo-Fenton conditions was also evaluated.

2. Experimental

2.1. Chemicals

Acetic and formic acids were analytical grade supplied by Merck. Pyruvic, maleic and oxalic acids were analytical grade purchased from Fluka. Reagent grade 33% (w/v) H_2O_2 was supplied by Panreac. Anhydrous sodium sulphate, used as background electrolyte, and pentahydrated ferric sulphate, used as catalyst, were analytical grade from Fluka and Aldrich, respectively. All solutions were prepared with high-purity water obtained from a Millipore Milli-Q system (resistivity $> 18 \text{ M}\Omega \text{ cm}$ at 25°C). Their initial pH was adjusted to 3.0 with analytical grade sulphuric acid supplied by Merck. Other chemicals used were analytical grade from Panreac and Merck.

2.2. Batch recirculation flow plant

A scheme of the batch recirculation flow plant used for the degradation of 2.5 l of carboxylic acid solutions under steady conditions was reported elsewhere [14]. The same configuration with the electrochemical cell coupled to the solar photoreactor was always used for the sake of comparison, although in the dark experiments the plant was covered with an opaque plastic for avoiding sunlight effects. The solution was introduced in a reservoir and continuously recirculated by the system with a peristaltic pump at a liquid flow rate of 200 l h^{-1} , being its temperature maintained at 35°C by two heat exchangers. The undivided filter-press electrochemical cell was equipped with a BDD thin film deposited on a conductive Si sheet from Adamant as anode and a stainless steel (AISI 304 grade) sheet as cathode. The contact area of both electrodes with the liquid was 20 cm^2 ($5 \text{ cm} \times 4 \text{ cm}$) and their separation was 1.2 cm. In the AO experiments, the current was supplied by an Agilent 6552A dc power supply, which directly displayed the applied cell voltage. The solar photoreactor was a polycarbonate box of $24 \text{ cm} \times 24 \text{ cm} \times 2.5 \text{ cm}$ (irradiated volume of 600 ml), connected to the liquid outlet of the cell. It was built-up with a mirror at the bottom and inclined 30° from the horizontal to better collect the direct sun rays [47].

Solutions containing 50 mg l^{-1} TOC of each carboxylic acid and $0.1 \text{ M Na}_2\text{SO}_4$ of pH 3.0 were always degraded in the batch recirculation flow plant. The pH value of 3.0 was chosen since it is close to the optimum pH of 2.8 for Fenton reaction (1) [22]. Chemical treatments with 1.0 mM Fe^{3+} and/or $20 \text{ mM H}_2\text{O}_2$ in the dark or under solar irradiation were carried out to clarify the influence of the different catalysts. All electrochemical degradations by AO with and without 1.0 mM Fe^{3+} in the dark or under sunlight were made at constant current density of 50 mA cm^{-2} , with a cell voltage of $8.1 \pm 0.2 \text{ V}$. No significant change in solution pH was found during all the chemical, photochemical and electrochemical trials performed. Solar experiments were carried out in sunny and clear days during June–August of 2007 and July of 2008 in our laboratory of Barcelona (latitude: $41^\circ 21' \text{N}$, longitude: $2^\circ 10' \text{E}$) with a decay in solar irradiation intensity from about 1000 W m^{-2} at noon to 400 W m^{-2} at 17 h, yielding an average UV irradiation intensity (UVB from 300 to 315 nm and mainly UVA at higher wavelengths up to 400 nm) close to 15 W m^{-2} , as measured by the university weather station.

Before the electrochemical treatment of each carboxylic acid, the surface of BDD was cleaned by electrolyzing 2.5 l of $1 \text{ M H}_2\text{SO}_4$ at 25 mA cm^{-2} for 4 h. After each trial with 1.0 mM Fe^{3+} , 2.5 l of 0.1 M HCl were recirculated through the flow plant for 2 h to remove the traces of this ion and further, it was similarly rinsed several times with Milli-Q water to become operative again.

2.3. Apparatus and analysis procedures

The pH of starting and treated solutions was measured with a Crison 2000 pH-meter. The concentration of H₂O₂ in electrolyzed solutions and in the chemical trials was determined from the light absorption of the Ti(IV)-hydrogen peroxide coloured complex at $\lambda = 408$ nm at pH ca. 1 [48]. These measurements were performed with a Unicam UV/vis UV4 spectrophotometer thermostated at 25 °C.

For chromatographic and TOC analysis, 7 ml samples were withdrawn from treated solutions and 0.05 ml of 6 M NaOH were added to obtain a pH close to 11 for stopping possible degradation reactions. The resulting solutions were then filtered with Whatman 0.45 μ m PTFE filters before measurements. Carboxylic acids were detected by ion-exclusion HPLC chromatography using a Waters 600 HPLC liquid chromatograph fitted with a Bio-Rad Aminex HPX 87H, 300 mm \times 7.8 mm (i.d.), column at 35 °C, and coupled with a Waters 996 photodiode array detector selected at $\lambda = 210$ nm. This analysis was carried out by injecting 20 μ l aliquots into the chromatograph and circulating 4 mM H₂SO₄ at 0.6 ml min⁻¹ as mobile phase. Under these conditions, chromatograms exhibited well-defined absorption peaks for oxalic, maleic, pyruvic, formic and acetic acids at retention time of 6.5, 8.0, 8.9, 13.6 and 14.9 min, respectively. The time-course of these acids was followed by determining their concentration via calibration with external standards.

The extent of the mineralization process in the chemical and electrochemical trials was monitored by the decay of the solution TOC determined with a Shimadzu 5050 TOC analyzer. Reproducible TOC values, with an accuracy of $\pm 1\%$, were always obtained by injecting 50 μ l aliquots into the above analyzer using the standard non-purgeable organic carbon method. From these data, the mineralization current efficiency (MCE) for each electrolyzed solution at a given time t (h) was calculated from Eq. (5) [14]:

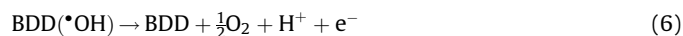
$$\text{MCE (\%)} = \frac{nFV_s \Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 mIt} \times 100 \quad (5)$$

where n is the number of electrons consumed in the mineralization process of each carboxylic acid, F is the Faraday constant ($=96,487$ C mol⁻¹), V_s is the solution volume (l), $\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC decay (mg l⁻¹), 4.32×10^7 is a conversion factor for units homogenisation ($=3600$ s h⁻¹ \times 12,000 mg of carbon mol⁻¹), m is the number of carbon atoms in each carboxylic acid and I is the applied current (A). The overall mineralization to CO₂ is accomplished with $n = 2$ for formic (HCOOH) and oxalic (COOH-COOH) acids, $n = 8$ for acetic (CH₃-COOH) acid, $n = 10$ for pyruvic (CH₃-CO-COOH) acid and $n = 12$ for maleic (COOH-CH=CH-COOH) acid.

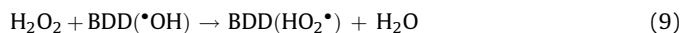
3. Results and discussion

3.1. Accumulation of electrogenerated H₂O₂ in the batch recirculation flow plant

The treatment of carboxylic acid solutions of pH 3.0 by AO involves the generation of a variety of ROS and other species at the BDD anode. Under our experimental conditions, the current density of 50 mA cm⁻² applied to the BDD/stainless steel cell of the flow plant is high enough to oxidize water to BDD([•]OH) from reaction (4), which can then be lost by parasitic reactions such as oxidation to O₂ (in primis) by reaction (6) or dimerization to H₂O₂ by reaction (7) [34–37]:



H₂O₂ thus produced is not inert and can be anodically oxidized to O₂ from overall reaction (8) or can react with BDD([•]OH) to yield hydroperoxyl radical (HO₂[•]) from reaction (9):



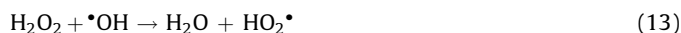
Apart from the generation of H₂O₂ and HO₂[•], other ROS such as ozone can be formed from total reaction (10) and weak oxidizing species such as peroxodisulfate (S₂O₈²⁻) ion can be generated by oxidation of SO₄²⁻ ion from the electrolyte via reaction (11) [34,36,37]:



Under these conditions, carboxylic acids are expected to be mainly mineralized with the strongest oxidant BDD([•]OH). When 1.0 mM Fe³⁺ is added to the solution of pH 3.0, a large proportion of Fe(III)-carboxylate complexes are formed, which remained in equilibrium with free Fe³⁺ and Fe(OH)²⁺. The former species can then be oxidized by BDD([•]OH), whereas the latter two species can be reduced at the cathode to Fe²⁺, e.g. by reaction (12) [16]:



The simultaneous presence of regenerated Fe²⁺ from reactions (2) and (12) and electrogenerated H₂O₂ from reaction (7) then allows the production of [•]OH via Fenton reaction (1) in the dark, which can also destroy in parallel the organic matter in solution. This process is expected to be more significant when the solution is irradiated with sunlight in the coupled solar photoreactor because of the much greater production of [•]OH and regeneration of Fe²⁺ induced by photo-Fenton reaction (3) and/or the additional photolysis of some Fe(III)-carboxylate complexes. However, some proportion of homogeneous [•]OH is consumed in parasitic reactions with chemical scavengers such as H₂O₂ from reaction (13) with $k_2 = 2.7 \times 10^7$ M⁻¹ s⁻¹ [49], Fe²⁺ from reaction (14) with $k_2 = 4.3 \times 10^8$ M⁻¹ s⁻¹ [50] and HO₂[•] from reaction (15) with $k_2 = 6.6 \times 10^9$ M⁻¹ s⁻¹ [51]:



Taking into account the expected complexity of the AO process, a first set of experiments was made in the batch recirculation flow plant to check the electrogeneration and accumulation of H₂O₂ in a 0.1 M Na₂SO₄ solution with and without Fe³⁺, carboxylic acids and sunlight. Fig. 1 shows a slow, but gradual accumulation of H₂O₂ up to a concentration of 1.46 mM during 300 min of electrolysis of the background electrolyte at 50 mA cm⁻². This tendency indicates that H₂O₂ is more rapidly produced from reaction (7) than consumed from reactions (8) and (9), suggesting that its accumulation could form [•]OH in the bulk using the Fe³⁺/Fe²⁺ system. This hypothesis was confirmed by electrolyzing the background electrolyte with 1.0 mM Fe³⁺ in the dark. As can be seen in Fig. 1, the H₂O₂ concentration in the medium undergoes a significant decrease under these conditions, only reaching a value of 0.70 mM at 300 min, which can be associated with its additional destruction by reactions (1) and (2). Fig. 1 also reveals the existence of lower H₂O₂ loss during the comparative electrolysis of 50 mg l⁻¹ TOC of pyruvic or oxalic acid with 1.0 mM Fe³⁺ operating in the dark. This behaviour can be ascribed to the presence of less free Fe³⁺ in the medium as a result of the competitive formation of

Fe(III)-carboxylate complexes, thus decreasing the rate of reactions (1) and (2) and enhancing H_2O_2 accumulation. In contrast, H_2O_2 is much more quickly destroyed in the electrolyzed pyruvic acid solution with 1.0 mM Fe^{3+} under solar irradiation, as expected if a larger quantity of Fe^{2+} is continuously produced from photo-Fenton reaction (3) that destroys greater amount of H_2O_2 via Fenton reaction (1). However, this trend is not observed in Fig. 1 for the electrolyzed oxalic acid solution with 1.0 mM Fe^{3+} since a similar H_2O_2 content is accumulated in the dark and under solar irradiation, probably due to its extra generation during the photolysis of Fe(III)-oxalate ions in the latter conditions [30–33].

The above results are indicative of a partial removal of accumulated H_2O_2 during the electrolysis of carboxylic acids with Fe^{3+} in the dark and under solar irradiation, producing $\cdot\text{OH}$ via Fenton reaction (1) and/or photo-Fenton reaction (3), which could accelerate the destruction of organics. To better clarify the synergistic effect of Fe^{3+} and/or sunlight in the AO process, the chemical and photochemical degradations of carboxylic acid solutions in the batch recirculation flow plant was studied, as discussed in subsection below.

3.2. Decay of carboxylic acids under Fenton-like and solar photo-Fenton conditions

Fig. 2 presents the time-course of the concentration of formic, oxalic, acetic, pyruvic and maleic acids during the different chemical and photochemical experiments performed in the batch recirculation flow plant without applying current to the electrochemical cell. In the trials with H_2O_2 , a high concentration of 20 mM of this compound (at least three times greater than that needed for the total mineralization of carboxylic acids) was added to the starting solutions to ensure the fast generation of $\cdot\text{OH}$ via reactions (1) and/or (3). It was found that the H_2O_2 content in solution did not vary under solar irradiation, decayed very slowly under Fenton-like conditions (with 1.0 mM Fe^{3+} in the dark) and was totally removed from 90 min for oxalic acid to 240 min for pyruvic acid using solar photo-Fenton (with 1.0 mM Fe^{3+} under solar irradiation).

A similar behaviour can be observed for 50 mg l⁻¹ TOC solutions of formic (Fig. 2a) and maleic (Fig. 2e) acids in the different conditions tested. Note that Fe(III)-formate and Fe(III)-maleate complexes are not photodegraded by sunlight when 1.0 mM Fe^{3+} is added to the medium, whereas the corresponding

free acids are very slowly removed up to 9% as maximum in 240 min in presence of 20 mM H_2O_2 in the dark and/or under solar irradiation. The combination of 1.0 mM Fe^{3+} and 20 mM H_2O_2 in the dark causes the fast disappearance of the Fe(III) complexes of formic and maleic acids in 90 and 40 min, respectively, mainly by their oxidation with $\cdot\text{OH}$ formed via Fenton-like process. When the solution is also irradiated with sunlight, Fig. 2a and e show a quicker destruction of the corresponding Fe(III)-formate and Fe(III)-maleate complexes, which are completely removed in 75 and 10 min, respectively, as expected by the synergistic action of photo-Fenton reaction (3) producing more amount of oxidant $\cdot\text{OH}$. The same tendency can be observed in Fig. 2c for Fe(III)-acetate complexes, although in this case the destruction rate of these species with $\cdot\text{OH}$ is so small that only allows the removal of 37 and 40% of the starting acid under Fenton-like and solar photo-Fenton conditions, respectively. It is also noticeable that acetic acid and its Fe(III) complexes are neither photolyzed by sunlight nor oxidized with H_2O_2 (see Fig. 2c).

A much greater action of solar irradiation was found for oxalic acid, as expected from previously reported results [26–28,30–33]. As illustrated in Fig. 2b, Fe(III)-oxalate species formed in 50 mg l⁻¹ TOC of oxalic acid and 1.0 mM Fe^{3+} are very quickly photodecomposed with sunlight, disappearing in 210 min. In contrast, this acid does not react with H_2O_2 and its Fe(III) complexes are not oxidized with $\cdot\text{OH}$ formed under Fenton-like conditions. Direct irradiation without Fe^{3+} only causes a slight reduction of oxalic acid in absence and presence of 20 mM H_2O_2 . Fig. 2b also depicts an enhancement of the destruction of Fe(III)-oxalate complexes in solar photo-Fenton, with total removal in 120 min. This can be related to the formation of a larger proportion of photoreactive species in presence of H_2O_2 , probably because the higher amount of Fe^{2+} produced by photo-Fenton reaction (3) is more rapidly converted into Fe^{3+} by Fenton reaction (1).

Fig. 2d shows higher chemical and photochemical reactivity for 50 mg l⁻¹ TOC of pyruvic acid. This compound is not directly photolyzed with sunlight, although it can be completely removed in 180 min with 20 mM H_2O_2 . In addition, Fe(III)-pyruvate complexes generated by adding 1.0 mM Fe^{3+} are completely photolyzed at approximately the same time. Results obtained for Fenton-like and solar photo-Fenton trials are not shown in Fig. 2d because in both cases the starting acid disappeared very rapidly from the medium, in less than 1 min. This proves that Fe(III)-pyruvate species react very quickly with $\cdot\text{OH}$ in the former process and their destruction is strongly enhanced in the latter one owing to their parallel photodecomposition.

The above findings suggest that the AO process of each carboxylic acid can be largely affected by Fe^{3+} and/or solar irradiation. It should also be noted that the HPLC analysis of chemical and photochemical degraded solutions allowed the identification of some acid intermediates. It was thus found that: (i) formic acid is produced from maleic acid, (ii) oxalic acid is generated from acetic and maleic acids and (iii) acetic acid is formed from pyruvic acid. The same intermediates were detected in the AO experiments, as will be described below.

3.3. Decay of carboxylic acids by AO in presence and absence of Fe^{3+} and sunlight

Solutions of 50 mg l⁻¹ TOC of each carboxylic acid at pH 3.0 were further degraded in the batch recirculation flow plant by applying a current density of 50 mA cm⁻² to the BDD/stainless steel cell. Three comparative experiments were carried out involving: (i) direct AO, (ii) AO with addition of 1.0 mM Fe^{3+} to the solution and (iii) AO with 1.0 mM Fe^{3+} coupled to solar irradiation. In each trial, the decay of substrate concentration was

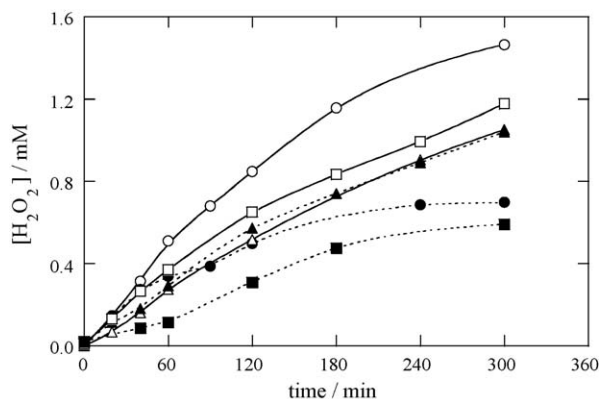


Fig. 1. Concentration of accumulated H_2O_2 with time during the electrolysis of 2.5 l of 0.1 M Na_2SO_4 solutions of pH 3.0 recirculating through a flow plant with a BDD/stainless steel cell with electrodes of 20 cm² area coupled to a solar photoreactor with 600 ml irradiated volume. Electrolyte (○) alone and with (●) 1.0 mM Fe^{3+} , 1.38 mM pyruvic acid and 1.0 mM Fe^{3+} (□) in the dark and (■) under solar irradiation, and 2.08 mM oxalic acid and 1.0 mM Fe^{3+} (△) in the dark and (▲) under solar irradiation. Operation conditions: 50 mA cm⁻², 35 °C and liquid flow rate of 200 l h⁻¹.

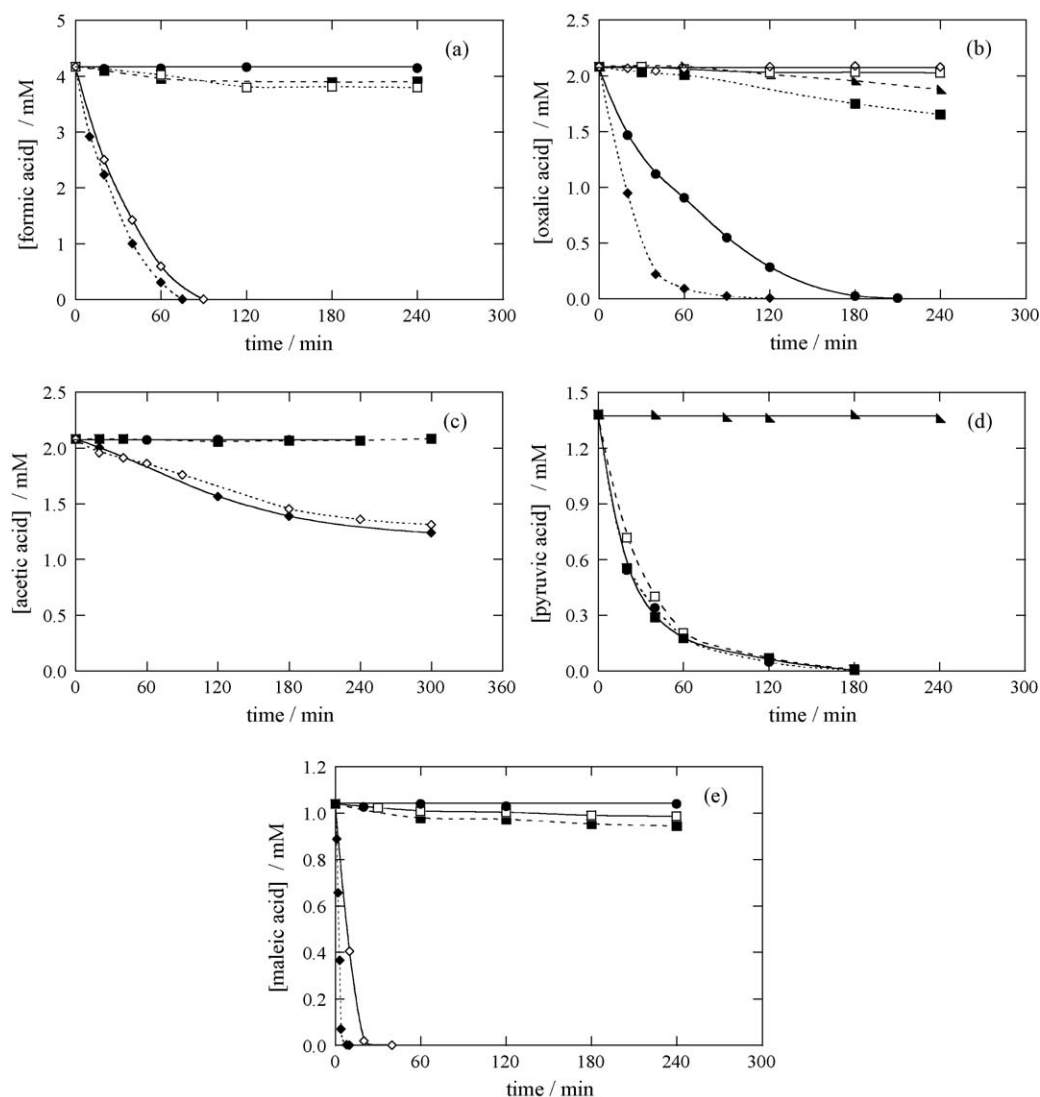


Fig. 2. Evolution of carboxylic acid concentration with time for 2.5 l solutions in 0.1 M Na₂SO₄ of pH 3.0 in the batch recirculation flow plant at 35 °C and liquid flow rate of 200 l h⁻¹. Carboxylic acid: (a) 4.17 mM formic, (b) 2.08 mM oxalic, (c) 2.08 mM acetic, (d) 1.38 mM pyruvic and (e) 1.04 mM maleic. Treatment: (▲) solar irradiation, (●) 1.0 mM Fe³⁺ under solar irradiation, (□) 20 mM H₂O₂ in the dark, (■) 20 mM H₂O₂ under solar irradiation, (◇) 20 mM H₂O₂ and 1.0 mM Fe³⁺ in the dark (Fenton-like conditions) and (◆) 20 mM H₂O₂ and 1.0 mM Fe³⁺ under solar irradiation (solar photo-Fenton conditions).

followed by ion-exclusion HPLC. The results obtained are presented in Fig. 3.

An increasing removal of formic, pyruvic and maleic acids from AO, AO with 1.0 mM Fe³⁺ and solar photoassisted AO with 1.0 mM Fe³⁺ can be observed in Fig. 3a, d and e, respectively. Fig. 3a shows that after 300 min of electrolysis, formic acid is reduced by 79% in direct AO, whereas its Fe(III) complexes attain higher removal of 84% in AO with 1.0 mM Fe³⁺ and 90% in solar photoassisted AO with 1.0 mM Fe³⁺. This trend is more apparent for pyruvic acid in Fig. 3d, because it is completely removed in about 300, 180 and 90 min for the above treatments. Similarly, overall disappearance of maleic acid takes place at ca. 240 min with 1.0 mM Fe³⁺ and at 150 min with additional solar irradiation, but it is only reduced by 68% after 300 min of direct AO (see Fig. 3e). These results prove that formic, pyruvic and maleic acids are mainly oxidized with BDD(•OH) produced from reaction (4), whereas their Fe(III) complexes are more rapidly destroyed in the dark by additional •OH predominantly formed via Fenton-like process, in agreement with chemical experiments reported in Fig. 2. The faster decay of these complexes in solar photoassisted AO with 1.0 mM Fe³⁺ corroborates the synergistic action of sunlight producing more quantity of •OH via

Fenton reaction (1) induced by photo-Fenton reaction (3), according to their photochemical results of Fig. 2. The larger influence of this method on the decay of Fe(III)-pyruvate species can then be associated with their additional photolysis, as shown in the experiments of Fig. 2d.

A quite different behaviour was found in the comparative treatments of oxalic acid. Fig. 3b shows that this acid undergoes a slow decay in direct AO because its concentration only drops about 50% after 300 min of electrolysis. Since photochemical trials of Fig. 2b depict a slight increase in the decay of free oxalic acid under solar irradiation, an additional solar photoassisted AO treatment without Fe³⁺ was comparatively made. The results of this trial presented in Fig. 3b clearly confirm that sunlight enhances its destruction, decreasing its concentration to 65% at 300 min. In contrast, when 1.0 mM Fe³⁺ is added to the solution in the dark, the oxidation of Fe(III)-oxalate complexes is strongly inhibited leading to a concentration reduction of 19% at the same time. Note that several authors [40,42,46] have reported that at low pH the AO process of oxalic acid at BDD is determined by the competition between direct charge transfer and reaction with BDD(•OH) formed from reaction (4). In this way, the strong inhibition of

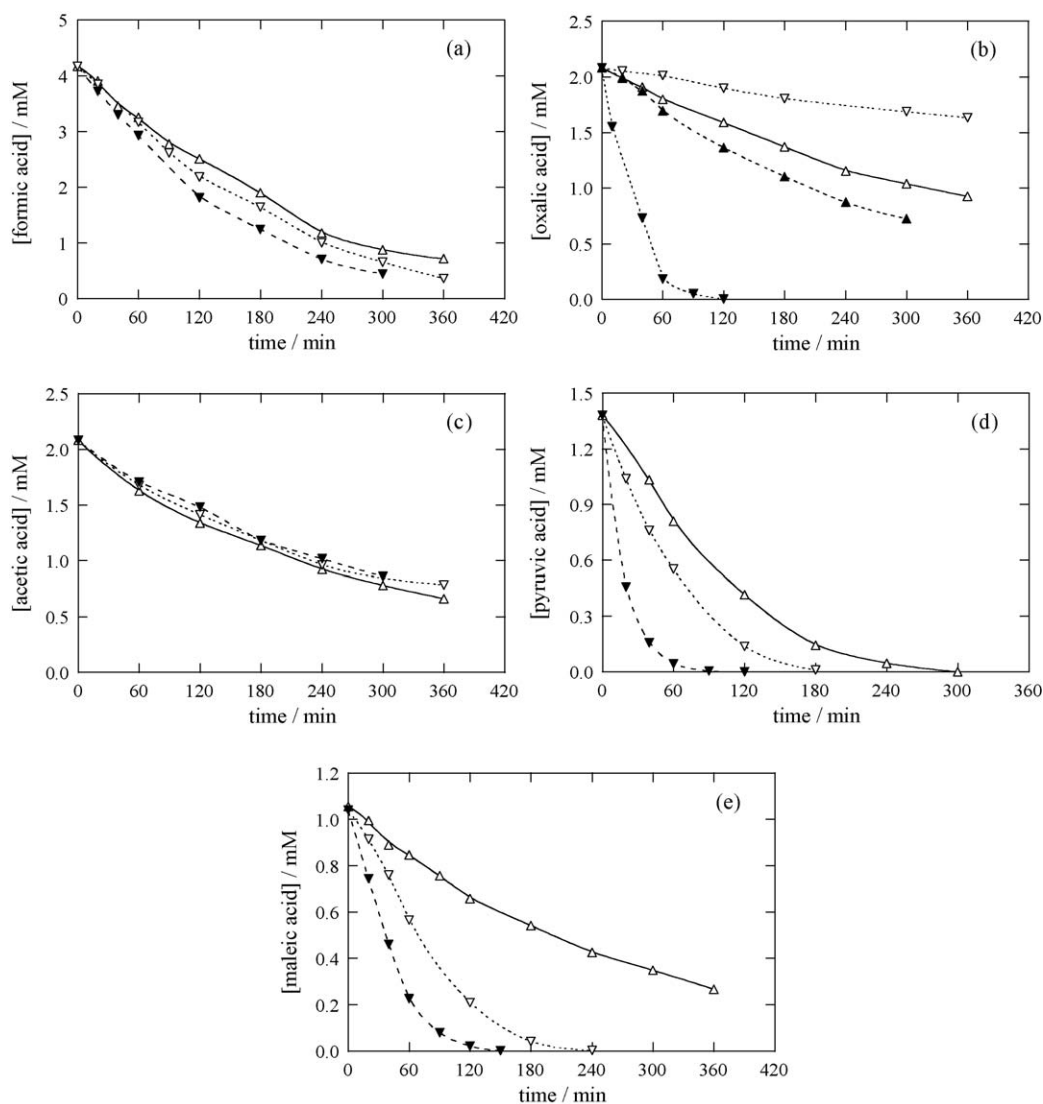


Fig. 3. Decay of carboxylic acid concentration for the degradation of 2.5 l solutions in 0.1 M Na₂SO₄ of pH 3.0 by (△) anodic oxidation (AO) in the dark, (▲) AO under solar irradiation, (▽) AO with 1.0 mM Fe³⁺ in the dark and (▼) AO with 1.0 mM Fe³⁺ under solar irradiation using the batch recirculation flow plant at 50 mA cm⁻², 35 °C and liquid flow rate of 200 l h⁻¹. Compound: (a) 4.17 mM formic, (b) 2.08 mM oxalic, (c) 2.08 mM acetic, (d) 1.38 mM pyruvic and (e) 1.04 mM maleic acids.

the oxidation of their Fe(III) complexes in AO suggests that they can only be destroyed very slowly by direct charge transfer at the anode, since they can not react with •OH (see Fig. 2b) and hence, neither with BDD(•OH). Fig. 3b also shows that AO with 1.0 mM Fe³⁺ under solar irradiation causes very fast removal of these complexes disappearing in 120 min as a result of their quick photodecomposition, as expected from results given in Fig. 2b. The presence of Fe³⁺ in the medium is then only effective for accelerating oxalic acid removal when it is combined with sunlight.

In the case of acetic acid, however, any synergistic effect of Fe³⁺ and sunlight on its decay rate was observed. As illustrated in Fig. 3c, this acid even undergoes slightly slower removal under the action of these catalysts than in their absence. After 300 min of treatment, for example, 62% of acetic acid is destroyed by direct AO, whereas it diminishes to 58% by solar photoassisted AO with 1.0 mM Fe³⁺. The effect of sunlight is rather insignificant, as expected from the fact that Fe(III)-acetate complexes are not photolyzed (see Fig. 2c). Recently, Kapalka et al. [44] demonstrated that acetic acid only reacts with BDD(•OH), although its adsorption on the BDD surface causes its autoinhibition. Our results suggest that Fe(III)-acetate complexes can be adsorbed even in larger

extent on BDD than the free acid and then, they are oxidized at lower rate predominantly with •OH generated from reactions (1) and/or (3).

The above concentration decays for all acids fit to a kinetic equation related to a pseudo-first-order reaction, except for the solar photoassisted AO treatment of oxalic acid with Fe³⁺ in which the predominant reaction is the photolysis of its Fe(III) complexes. This agrees with the fact that in all the other cases, the main oxidant is BDD(•OH) formed from reaction (4) and/or •OH produced from reactions (1) and/or (3) depending on the method tested. The mean value of the pseudo-first-order rate constant (k_1) within a 95% confidence interval for each acid in each treatment thus obtained is summarized in Table 1. According to these k_1 -values, the tested acids are more quickly oxidized with BDD(•OH) in direct AO in the sequence: oxalic < acetic < maleic < formic < pyruvic. The relative order of k_1 varies in solar photoassisted AO with 1.0 mM Fe³⁺, where maleic acid is more rapidly removed than formic acid, but much more slowly than pyruvic acid. As expected, the k_1 -value for acetic acid even slightly decreases in the latter procedure. These findings indicate that the combination of Fe³⁺ and sunlight with AO for wastewater remediation is limited by the kind of carboxylic acid generated.

Table 1

Pseudo-first-order rate constant (k_1) mean value within a 95% confidence interval determined for the decay of 50 mg l^{-1} TOC of carboxylic acids in 2.5 l solutions with $0.1 \text{ M Na}_2\text{SO}_4$ at pH 3.0 and 35°C by different anodic oxidation (AO) processes using a batch recirculation flow plant with a BDD/stainless steel cell containing electrodes of 20 cm^2 area at 50 mA cm^{-2} coupled to a solar photoreactor of 600 ml irradiated volume operating at liquid flow rate of 200 l h^{-1} .

| Carboxylic acid | $k_1 \times 10^4 (\text{s}^{-1})$ | | |
|-----------------|-----------------------------------|--|--|
| | AO in the dark | AO with 1.0 mM Fe^{3+} in the dark | AO with 1.0 mM Fe^{3+} under solar irradiation |
| Formic | 0.71 ± 0.03 | 0.85 ± 0.06 | 1.13 ± 0.09 |
| Oxalic | 0.39 ± 0.02 | 0.12 ± 0.02 | — ^a |
| Acetic | 0.57 ± 0.03 | 0.54 ± 0.01 | 0.51 ± 0.04 |
| Maleic | 0.63 ± 0.01 | 2.06 ± 0.10 | 4.45 ± 0.67 |
| Pyruvic | 1.75 ± 0.43 | 2.65 ± 0.38 | 9.29 ± 0.40 |

^a No linear correlation was obtained.

3.4. TOC abatement and mineralization current efficiency

The mineralization process of the above carboxylic acids solutions in the different electrochemical methods tested was studied from their TOC abatement. From these data, the comparative MCE values were determined using Eq. (5) with the corresponding n -value for the total transformations of each acid into CO_2 . Note that there is some controversy in the literature about the evolution of some carboxylic acids in AO with a BDD anode. For example, it has been reported that the oxidation of acetic acid gives either oxalic and formic acids [38] or ethane and methanol [45] as main intermediates. In the case of maleic acid, direct transformation into CO_2 [39] or oxidation to acetic and oxalic acids as intermediates [46] has been described. For this reason, TOC decay for electrolyzed solutions was compared with

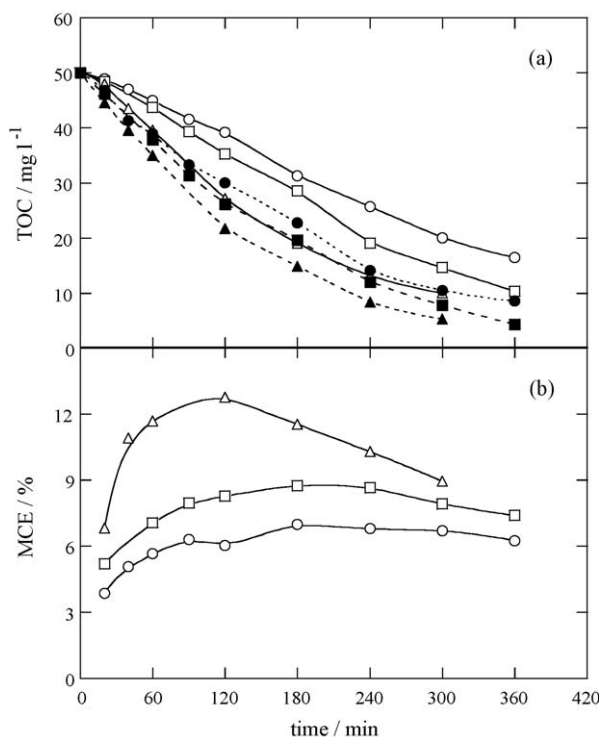


Fig. 4. (a) Change of TOC of 4.17 mM formic acid solutions in $0.1 \text{ M Na}_2\text{SO}_4$ of pH 3.0 (empty symbols) with electrolysis time in the batch recirculation flow plant at 50 mA cm^{-2} , 35°C and liquid flow rate of 200 l h^{-1} . The filled symbols represent the calculated TOC for the remaining formic acid concentration. Method: (○, ●) AO in the dark, (□, ■) AO with 1.0 mM Fe^{3+} in the dark and (△, ▲) AO with 1.0 mM Fe^{3+} under solar irradiation. (b) Mineralization current efficiency for the above experiments.

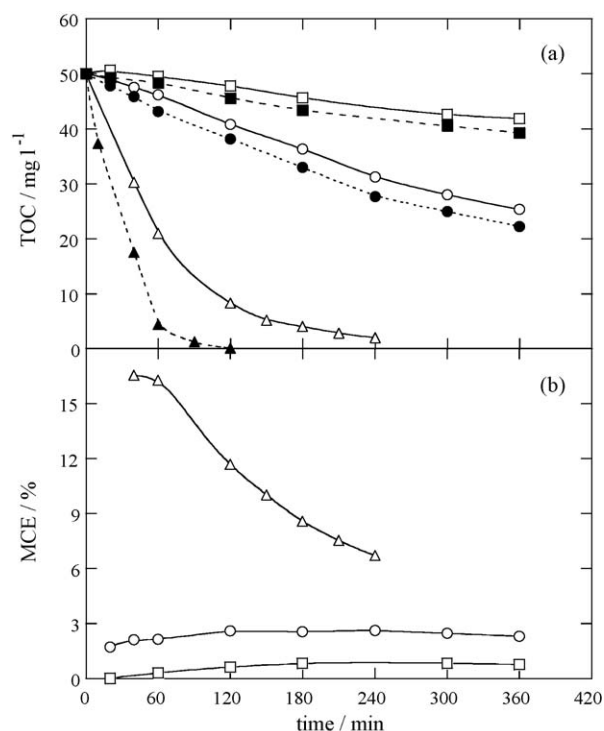


Fig. 5. (a) TOC removal of 2.08 mM oxalic acid solutions in $0.1 \text{ M Na}_2\text{SO}_4$ of pH 3.0 (empty symbols) using the batch recirculation flow plant at 50 mA cm^{-2} , 35°C and liquid flow rate of 200 l h^{-1} . The filled symbols denote the calculated TOC corresponding to the remaining oxalic acid concentration. Treatment: (○, ●) AO in the dark, (□, ■) AO with 1.0 mM Fe^{3+} in the dark and (△, ▲) AO with 1.0 mM Fe^{3+} under solar irradiation. (b) Mineralization current efficiency for the above trials.

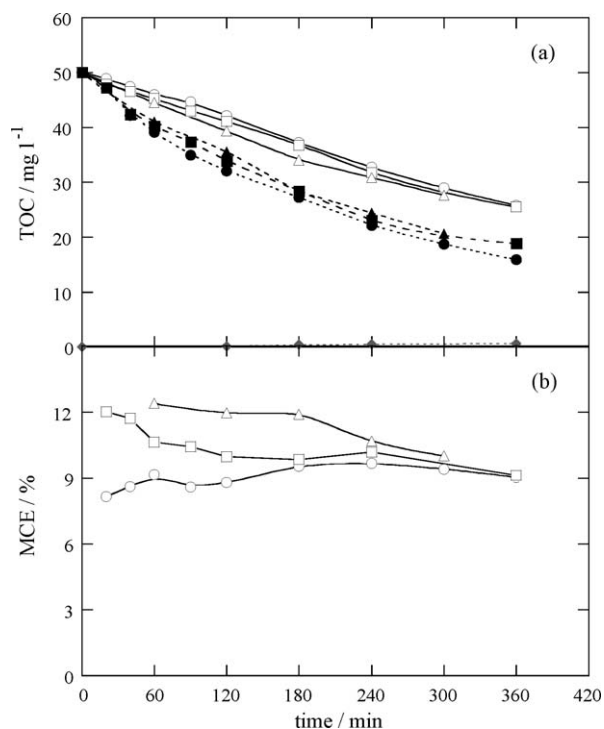


Fig. 6. (a) Variation of TOC of 2.08 mM acetic acid solutions in $0.1 \text{ M Na}_2\text{SO}_4$ of pH 3.0 (empty symbols) with electrolysis time in the batch recirculation flow plant at 50 mA cm^{-2} , 35°C and liquid flow rate of 200 l h^{-1} . The filled symbols correspond to the calculated TOC of the remaining acetic acid. Method: (○, ●) AO in the dark, (□, ■) AO with 1.0 mM Fe^{3+} in the dark and (△, ▲) AO with 1.0 mM Fe^{3+} under solar irradiation. (b) Evolution of TOC of oxalic acid detected as intermediate in AO with 1.0 mM Fe^{3+} in the dark. (b) Mineralization current efficiency for the above trials.

the theoretically calculated value from the remaining acid and its oxidation intermediates detected by HPLC in order to evaluate the evolution of organics during the mineralization process.

Fig. 4a shows a slow TOC removal for formic acid solutions with electrolysis time, which increases in the sequence: direct AO < AO with 1.0 mM Fe^{3+} < solar photoassisted AO with 1.0 mM Fe^{3+} . This trend is the same as found for its concentration decay (see Fig. 3a), indicating that greater mineralization is attained as the starting acid is more quickly destroyed. However, lower TOC abatement was determined from the remaining formic acid in electrolyzed solutions, as depicted in Fig. 4a, without detection of other acids as by-products. For example, after 300 min of AO with 1.0 mM Fe^{3+} under solar irradiation, TOC decreases to 9.9 mg l^{-1} , but 5.3 mg l^{-1} of them only correspond to unreacted formic acid and hence, the solution contains a small quantity of undetected organics equivalent to 4.6 mg l^{-1} TOC. Results of Fig. 4a also reveal much lower content of intermediates by combining Fe^{3+} and sunlight in comparison to direct AO. The synergistic effect of both catalysts producing more oxidant $\cdot\text{OH}$ under the action of photo-Fenton reaction (3) then favours the destruction of organic by-products and enhances the mineralization process. The fact that all formic acid or its Fe(III) complexes are not directly converted into CO_2 , can also be deduced from efficiencies given in Fig. 4b. A maximum MCE of 12.8% at 120 min is obtained for the most efficient method of solar photoassisted AO with 1.0 mM Fe^{3+} , suggesting an increasing generation of easily degradable intermediates at the early stages of this treatment, followed by a gradual decay in CO_2 formation at long electrolysis times due to the production of more difficultly oxidizable organics. This behaviour is less apparent in direct AO and AO with 1.0 mM Fe^{3+} with much lower efficiency because of their smaller ability to destroy intermediates with BDD($\cdot\text{OH}$) and/or $\cdot\text{OH}$ formed under Fenton-like conditions.

As expected from Fig. 3b, the solar photoassisted AO treatment of oxalic acid with 1.0 mM Fe^{3+} allows its overall mineralization. However, Fig. 5a illustrates that this degradation process leads to a large quantity of intermediates that are more slowly destroyed than Fe(III)-oxalate complexes. Thus, while these initial species disappear in 120 min, total conversion into CO_2 is achieved in about 240 min. This suggests that Fe(III)-oxalate complexes are rapidly photolyzed giving rise to organics that are rather mineralized under the action of $\cdot\text{OH}$ and/or BDD($\cdot\text{OH}$). The efficiency of this process progressively decreases from 16.5% at its early stages to 6.7% at 240 min (see Fig. 5b), as expected if lower quantity of organics is gradually mineralized. In contrast, a practically constant MCE of 2.5% can be observed in Fig. 5b for direct AO, a value higher than ca. 0.6% obtained for AO with 1.0 mM Fe^{3+} . This agrees with the constant and slow TOC abatement rate of oxalic acid or its Fe(III) complexes reported in Fig. 5a for such treatments, yielding a small proportion of organic intermediates, because all these compounds are mainly oxidized to CO_2 by direct charge transfer and/or with BDD($\cdot\text{OH}$), as stated above.

Fig. 6a illustrates the slow and quite similar TOC removal found for acetic acid in all methods, as expected from the practically equal decay rate of its concentration depicted in Fig. 3c. In all cases, TOC is reduced by 42–45% in 300 min, while the efficiency varies between 9 and 12% along the treatments (see Fig. 6b). A small oxalic acid concentration ($<0.6 \text{ mg l}^{-1}$ TOC) is only detected in AO with 1.0 mM Fe^{3+} , i.e., when its Fe(III) complexes are very slowly destroyed by direct charge transfer, as pointed out above. Oxalic acid or Fe(III)-oxalate complexes are then destroyed at the same rate as formed in direct AO or solar photoassisted AO with 1.0 mM Fe^{3+} by BDD($\cdot\text{OH}$) or sunlight, respectively. However, comparison of experimental TOC and the corresponding values related to remaining acetic acid from results of Fig. 6a allows concluding the generation of a large amount of other difficultly oxidizable organic

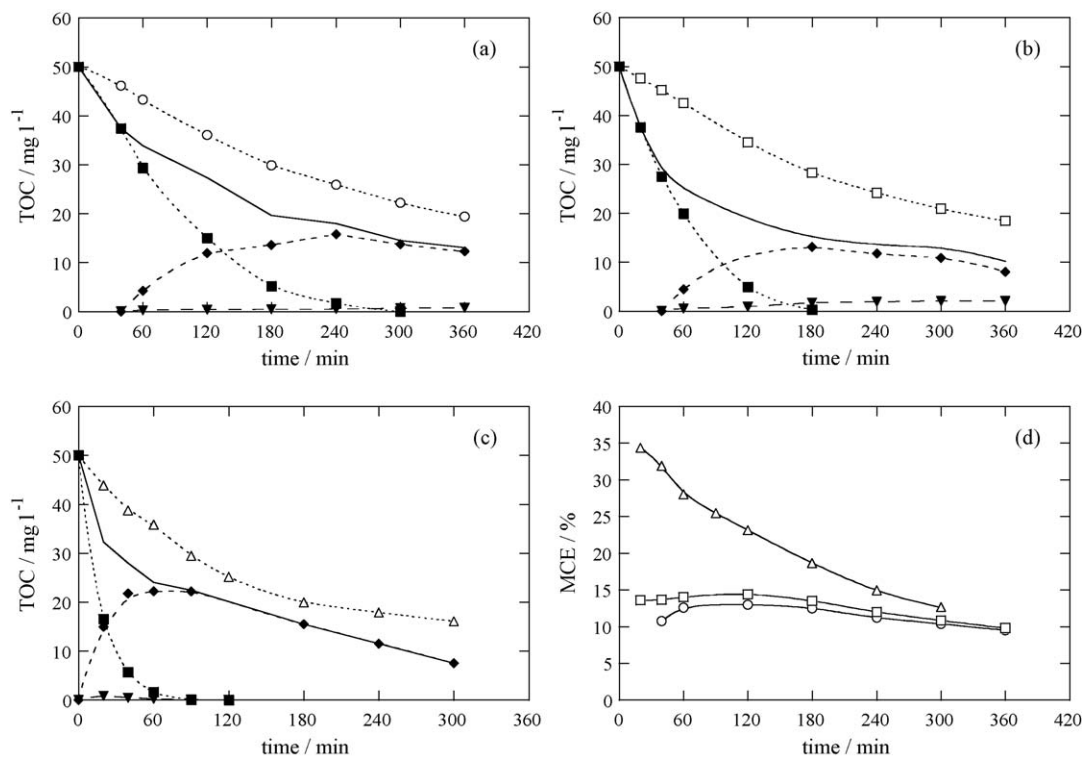


Fig. 7. (a–c) Change of TOC and (d) mineralization current efficiency with electrolysis time during the degradation of 1.38 mM pyruvic acid solutions in 0.1 M Na_2SO_4 of pH 3.0 by (○) AO in the dark, (□) AO with 1.0 mM Fe^{3+} in the dark and (△) AO with 1.0 mM Fe^{3+} under solar irradiation using the batch recirculation flow plant at 50 mA cm^{-2} , 35°C and liquid flow rate of 200 l h^{-1} . In plots (a–c), dashed lines correspond to the TOC of (■) the remaining pyruvic acid and the accumulated (◆) acetic and (▼) oxalic acids, whereas the solid line represents the total TOC obtained from detected carboxylic acids.

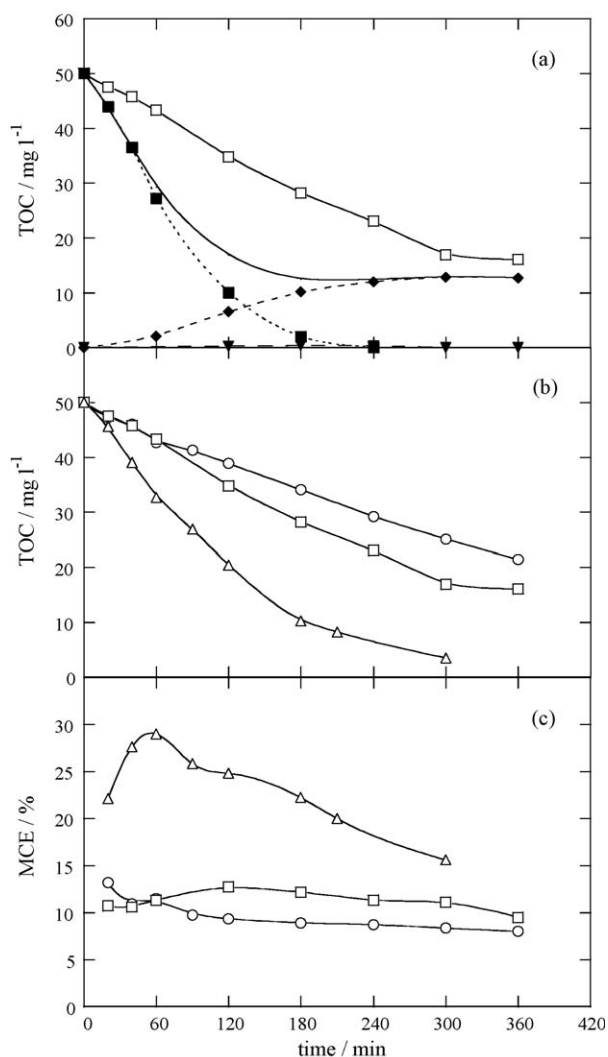


Fig. 8. (a) Time-course of TOC of (□) 1.04 mM maleic acid solution in 0.1 M Na₂SO₄ of pH 3.0, (■) the remaining maleic acid and the accumulated (◆) oxalic and (▼) formic acids during the AO degradation with 1.0 mM Fe³⁺ in the dark using the batch recirculation flow plant at 50 mA cm⁻², 35 °C and liquid flow rate of 200 l h⁻¹. The solid line gives the total TOC of detected carboxylic acids. (b) TOC removal and (c) mineralization current efficient for the maleic acid solution treated by (○) AO in the dark, (□) AO with 1.0 mM Fe³⁺ in the dark and (△) AO with 1.0 mM Fe³⁺ under solar irradiation.

intermediates, which attain contents as high as 10 mg l⁻¹ TOC after 300 min of electrolysis. One of these products could be methanol, as recently reported by Kapalka et al. [45]. Our results then indicate that acetic acid degradation is not influenced by the catalytic action of Fe³⁺ and sunlight on electrogenerated H₂O₂ in the AO process with BDD, being produced large quantities of refractory organics that prolong its overall transformation into CO₂.

The degradation of pyruvic acid takes place via acetic and oxalic acids as intermediates. The low reactivity of these by-products and their Fe(III) complexes with BDD(•OH) and •OH, together with the photostability of Fe(III)-acetate complexes, avoid its overall mineralization. This behaviour can be seen in Fig. 7a–c for direct AO, AO with 1.0 mM Fe³⁺ and solar photoassisted AO with 1.0 mM Fe³⁺, respectively. TOC decay is very rapid at the early stages of all electrolyses, being strongly enhanced when the removal rate of the Fe(III)-pyruvate species increases by the synergistic effect of Fe³⁺ and sunlight. However, TOC is much slowly removed when only intermediates remain in solution by prolonging electrolysis time. For example, the above methods lead to increasing TOC reductions

of 13.6, 15.1 and 29.3% at 60 min and 55.6, 58.2 and 67.9% at 300 min. The faster removal of the starting compound also favours the quicker formation and destruction of acetic acid or its Fe(III) complexes, which are always notably accumulated as main intermediates. Fig. 7a–c reveal the accumulation of other undetected by-products in large extent, along with small amounts of oxalic acid in all cases. Since the latter acid is produced in much larger extent than that expected from acetic acid oxidation (see Fig. 6a), it also comes from the degradation of other organics formed from pyruvic acid destruction. The much faster initial degradation of pyruvic acid by solar photoassisted AO with 1.0 mM Fe³⁺ is confirmed from MCE values given in Fig. 7d, which dramatically decrease from 34.6% at the early stages to 16.1% at 300 min as a result of the gradual generation of more recalcitrant and persistent by-products. In contrast, MCE values only vary between 10 and 14% for direct AO and AO with 1.0 mM Fe³⁺ because of the slower destruction of the organic matter, although the latter method is slightly more efficient.

A similar behaviour to pyruvic acid was found for maleic acid, although it attained almost overall mineralization after 300 min of AO with 1.0 mM Fe³⁺ under solar irradiation since easily degradable Fe(III)-oxalate and Fe(III)-formate complexes are generated as intermediates. The evolution of experimental TOC and the values related to acids detected in AO with 1.0 mM Fe³⁺ is presented in Fig. 8a. A reduction of 67.9% of the solution TOC in 360 min can be observed, while Fe(III)-maleate complexes disappear in 240 min giving rise to Fe(III)-oxalate species and a much minor proportion of other intermediates such as Fe(III)-formate complexes (<0.4 mg l⁻¹ TOC). All these organics are more rapidly destroyed in solar photoassisted AO with 1.0 mM Fe³⁺ allowing 93% of TOC abatement after 300 min of electrolysis (see Fig. 8b). In contrast, the slower removal of maleic, oxalic and formic acids by direct AO only leads to 49.8% of TOC abatement at the same time (see Fig. 8b). According to these results, Fig. 8c shows that higher efficiencies are always obtained when AO is combined with Fe³⁺ and sunlight, with a maximum value of 29.0% at 60 min.

The above results indicate that solar photoassisted AO treatment of organics in presence of Fe³⁺ can be useful when oxalic and formic acids are formed as ultimate carboxylic acids because their easier destruction under the action of Fenton, Fenton-like and/or photo-Fenton reactions largely enhances the mineralization process in comparison to direct AO. The performance of this combined method, however, decreases strongly when persistent acetic acid is generated in large extent during the degradation process, as in the case of pyruvic acid. The excess of Fe³⁺ in solution can be reused in further trials because it can be easily collected as Fe(OH)₃ precipitate by neutralizing at pH 7–8 before disposal of resulting wastewater.

4. Conclusions

It has been demonstrated that the synergistic action of Fe³⁺ and sunlight in the AO process favours a much faster destruction of formic, oxalic, pyruvic and maleic acids in comparison with direct AO, but not for acetic acid that disappears practically at the same rate in both cases. When these catalysts are used, Fe(III)-carboxylate complexes can be oxidized by direct charge transfer at the anode and/or by BDD(•OH), along with other two degradative ways involving either the production of oxidant •OH via Fenton and photo-Fenton reactions or their photodecomposition under solar irradiation. While the removal of Fe(III)-formate and Fe(III)-maleate complexes is enhanced by the former degradative way and Fe(III)-oxalate species are only photolyzed, both additional ways can accelerate the destruction of Fe(III)-pyruvate complexes. In contrast, acetic acid and its Fe(III)-complexes are transformed into CO₂ at similar rate in all methods.

The combined EAOP also allows a quicker conversion of Fe(III)-formate complexes into CO₂ and complete mineralization of starting oxalic acid. Maleic acid is degraded giving formic and oxalic acids and then, it undergoes almost total mineralization under the experimental conditions tested. The mineralization current efficiency for formic, oxalic and maleic acids is then much greater in the AO process combined with Fe³⁺ and sunlight than in the AO treatments with and without Fe³⁺ in the dark. The fact that pyruvic acid is mainly oxidized to acetic acid avoids its complete mineralization in the former procedure, although with a higher efficiency than for the other AO processes because of the more rapid conversion of Fe(III)-pyruvate complexes into persistent by-products. From these results, one can infer that the proposed solar photoassisted anodic oxidation with Fe³⁺ can be a useful environmentally friendly method for wastewater remediation when organics are degraded to oxalic and formic acids as ultimate carboxylic acids since their Fe(III) complexes are much more easily destroyed in this combined method than the corresponding acids in direct anodic oxidation. The formation of persistent acetic acid during the degradation process leads to a significant loss of its performance.

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